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~~Blue Light-emitting, ladder-type~~ Ladder-type and Blue Light-Emitting Polymer with Excellent Thermal Heat Stability

FIELD OF THE INVENTION

5 The present invention relates to luminescent polymer, specifically ladder-type
and blue light-emitting ~~polymer polymers~~ with excellent thermal ~~heat~~ stability, which
are prepared ~~polymerization, after grafting by~~ polymerization of blue luminescent ~~to~~
~~backbone polymers or after substituting luminescent monomers to styrene derivatives~~
monomer or grafting blue luminescent monomer to backbone polymer.

10

PRIOR ART

~~Polymers are~~ Polymer has been generally classified as ~~none~~ conductive and
~~are not used as the electronic materials~~ insulator. Recently, development
~~Development of~~ conducting polymers such as polyaniline, polypyrrole and
15 polythiophene has provided ~~excellent materials with the~~ high conductivity as same as
~~metals, light weight, and processability~~ metal. These polymers have advantages over
metal in aspects of light weight and processability.

The conjugated polymers with the electrical and optical characteristics have
20 been ~~are~~ used for the applications of anti-static materials, sensors, electrodes,
transistors, light-emitting materials, solar cell, smart cards, electronic newspapers,
and other display devices. The luminescence polymer ~~materials have~~ has been
extensively developed ~~extensively~~ since the electroluminescence with poly(1,4-
phenylenevinylene) was reported in Cambridge group in 1990 (Burroughes, J. H.;
25 Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P.
L.; Holmes, A. B. Nature 1990;347:539). The features of luminescence polymer are,

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The materials are in comparison with the inorganic materials, light weight, thin, self-luminescent, ~~mobile with~~ of low voltage, and have threshold voltage. These polymers also provide fast switching velocity, easy processability, low production cost, low dielectric constant, and most of all, prospect of various uses, making them as the
5 light-emitting materials for the information and communication technology of next generation. They provide the advantage of easy fabrication and controllable electrical and optical properties by the modification of their molecular structures. These properties allow them as the promising light-emitting materials for information and communication technology of the next generation.

10

The blue luminescent polymer employs ~~uses~~ aromatic groups ~~compounds~~ such as fluorene or spiro-fluorene as conjugated polymers of the backbone ~~polymers~~. Examples are polymers as described in U.S. Patents ~~Patent No.s of~~ 5593788, 5597890, 5763636, and 5900327. In U.S. Patent 5998045, the luminescent polymers ~~materials~~
15 are prepared ~~produced by the use of polymers copolymerized~~ copolymerization of fluorene and anthracene. The copolymers by the fluorene and aromatic compounds (for example, carbazole) are reported in German Patents ~~Patent No.s of~~ 198 46 766, 198 46 767, and 198 46 768. In U.S. Patent No. 6395410, ~~making an~~ electroluminescence devices are prepared with ~~is reported by mixing the~~ luminescent
20 ~~materials and transparent polymers. with low absorption in the visible light regions~~ (such as polycarbonate, polystyrene, polymethacrylate, polyvinylcarbazole). Recently, application research is under way for the organic semiconductor using a thin film (Appl. Phys. Lett. 80(6), 1088).

25

Much effort ~~Much improvements are~~ is needed as yet in the durability and brightness of the blue light-emitting polymers when they are applied to the

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luminescent devices. The ~~devices, the~~ main reason is being due to poor ~~their~~ thermal stability ~~instability~~. Heat causes molecular movement ~~movements of~~ polymers and generates fine particles or coagulates ~~the polymers~~. Heat generation ~~Generation of~~ heat increases in proportion to the ~~using~~ period of working time of the
5 electroluminescence devices, ~~decreasing their durability when the glass transition temperature and melting temperature are below 300 °C~~. The existing light-emitting polymers have the glass transition temperature at around 100 °C (Macromolecules; 1988; 31(4); 1099-1103) causing such ~~the above~~ problems.

10 SUMMARY OF THE INVENTION

Therefore, the inventors of the present invention intended to prepare the blue luminescent polymers with high melting point and ~~heat stability~~ with excellent thermal stability.

15 As a result, ~~as the~~ ladder-type blue light-emitting polymers that can completely satisfy the said ~~problems, the~~ problems were conceived. The present invention comprises ~~either polymerizing the polymers after grafting the polymerization of blue luminescent monomer or grafting blue luminescent monomer to backbone polymer~~ light-emitting monomers to their backbone or ~~polymerizing~~
20 ~~styrene monomers after addition of fluorene group to them~~.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1(a) is the conceptual picture of a conventional blue light-emitting polymer.

25 Fig. 1(b) is the conceptual picture of a ladder-type blue light-emitting polymer.

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Fig. 2 shows synthetic scheme of the ladder-type blue light-emitting polymer.

Fig. 3 shows ~~the~~ UV-VIS ~~spectrum~~ spectra.

Fig. 4 shows the photoluminescence ~~spectrum~~ spectra.

Fig. 5 shows the TGA of P1.

5 Fig. 6 shows the TGA of P2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides the preparation of ~~the heat stable and blue~~
10 thermally stable and blue light-emitting polymers. Novel luminescent polymers with
the ladder-type structure are proposed in order to make thermally ~~highly heat~~ stable
~~polymers differing from the existing luminescent polymers with the polymer, which~~
has a high glass transition ~~temperature around 100 °C. These polymers have high~~
~~glass transition~~ temperature, above 400 °C, and high temperature of 5%-weight loss,
15 above 450 °C, and ~~are~~ is easily soluble in ~~the organic solvents~~ solvent for thin film
applications. Herein, polystyrene as backbone enabling the production of thin films.
~~The backbone polystyrene~~ is transparent in the visible region, increases compatibility
with other polymers, inhibits molecular movement and increases thermal ~~the heat~~
stability.

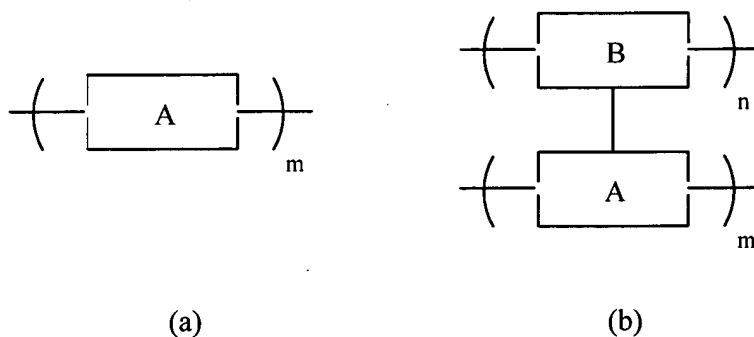
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The conventional polyfluorene and polyaryl polymers have the structure of
(a) as shown in Figure 1, and are movable at a higher ~~the figure 1. Their molecular~~
~~movement at a higher temperature is active, making it difficult to have the glass~~
~~transition~~ temperature above 100 °C. The ladder-type polymers of the invention
25 have a structural composition as shown in Figure 1 (b), ~~In figure 1(b)~~ where block A
is light-emitting part, ~~while~~ and block B is polystyrene ~~that~~. Polystyrene has excellent

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optical properties, high thermal ~~heat~~-stability and inhibits molecular movement. The polystyrene block is readily dissolved in solvent, and allows easy fabrication ~~the solvents readily, making it easy to fabricate thin film.~~

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~~Figure 1,~~ Figure 1: The conceptual picture of a conventional blue light-emitting polymer(a) and a ladder-type blue light-emitting polymer(b)

10

Therefore, the present invention provides the blue light-emitting polymer represented in Figure ~~he figure~~-1(b).

Wherein, A is selected from polyfluorene, polythiophene, polypyrrole, polycarbazole, polyphenylene, polyaniline, polypyridine; B is selected from
15 polystyrene, polypyrrol, polythiophene, polycarbonate, polyphenylene, polyaniline, polypyridine, polycarbazole; n is an integer of 5 to 100; and m is an integer of 2 to 100.

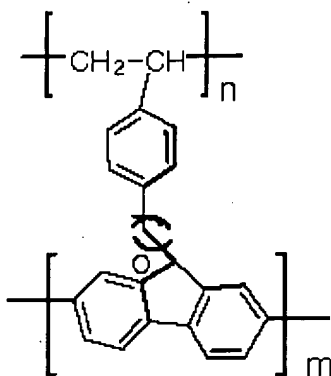
~~And, the~~ The blue light-emitting polymer can be represented by the following
20 formula 1.

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Wherein **A** is polyfluorene; **B** is polystyrene; n is an integer of 5 to 100; and m is an integer of 2 to 100.

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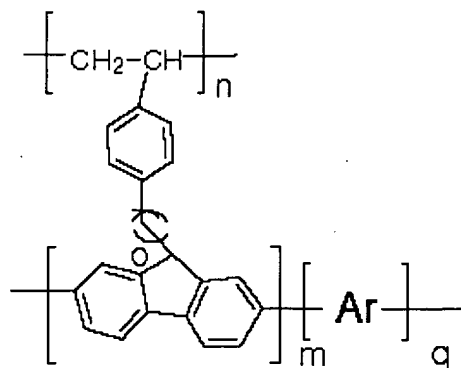


[Formula 1]

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And, the present invention provides the blue light-emitting polymers containing **Ar** compounds additionally represented in the formula 2

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[Formula 2]

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Wherein **Ar** is aromatic compounds such as fluorene, fluorene derivatives,

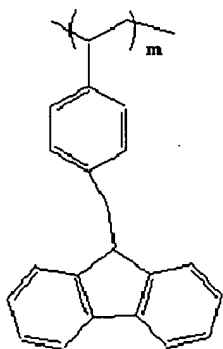
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benzene, benzene derivatives, thiophene, thiophene derivatives, carbazole, carbazole derivatives, pyridine or pyridine derivatives. Preferable, **B** is polystyrene with atactic or syndiotactic structure in the formula 1 or 2.

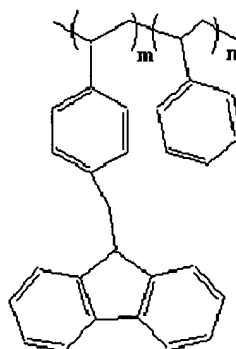
5 The ladder-type blue light emitting polymers described above can be synthesized in various methods.

 The first method comprises eliminating a hydrogen atom from C₉ position of fluorene or dibromofluorene using n-butyl lithium in tetrahydrofuran, grafting polyvinyl benzene chloride to it, and polymerizing aryl groups with the use of nickel
10 or iron catalyst.

 The second method comprises substituting chloride atom of vinyl benzene chloride with fluorene, polymerizing the styrene part, and polymerizing fluorene with nickel or iron catalyst. Other method includes polymerizing vinylfluorene, [formula 3], or copolymerizing styrene with vinylfluorene to make a polymer of [formula 4],
15 and polymerizing fluorene groups.



[Formula 3]



[Formula 4]

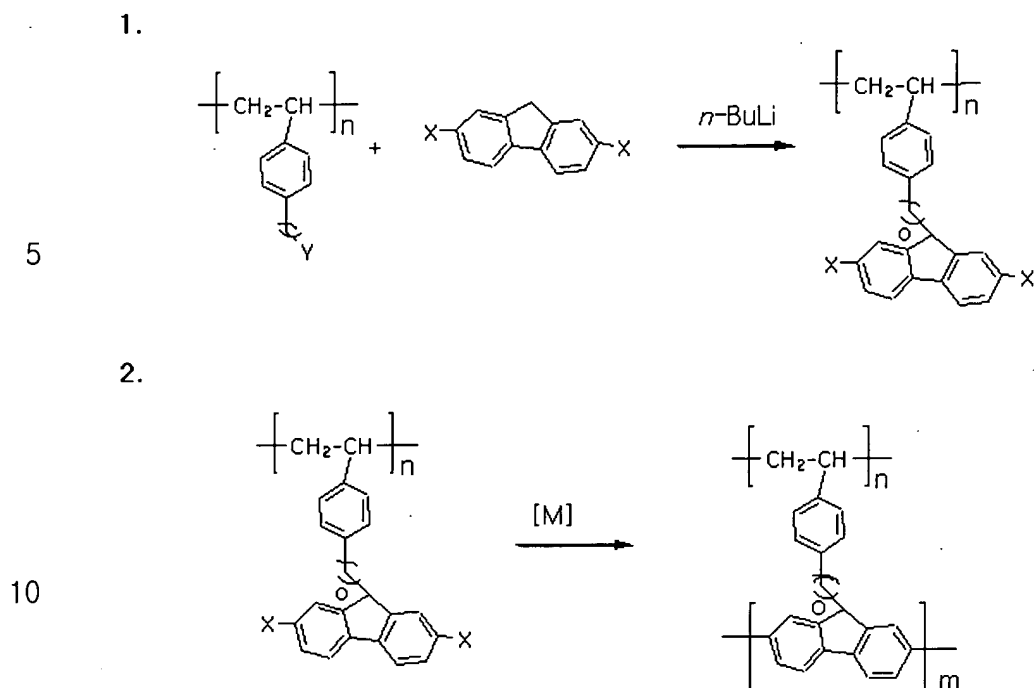


Figure 2: synthetic scheme of the ladder-type blue light-emitting polymer.

The polymers exhibited glass transitions (T_g), 422 °C for P1, 404 °C for P2, and 414 °C for P3, and no melting endotherms were found out. Syndiotacticity contributes the high glass temperature of P3 in spite of low molecular weight. Thermal decomposition temperatures at 5%-weight loss (T_d), 475 °C for P1, 448 °C for P2, and 233 °C for P3 were observed. The fluorescence peaks of P1, P2, P3 were observed at 401 nm, 416 nm and 415 nm, respectively. For the emission spectrum of P3, no shoulder or peak regarding of aggregation of polyfluorene was observed. Syndiotacticity, due to alternative configuration of fluorene, prevents a large Stoke's shift of the luminescence spectrum. In the UV-Visible spectrum of the polymer P1, λ_{max} is obtained at 362 nm (Fig. 3). For P2, λ_{max} is also obtained at 362 nm. The emissions of P1 and P2 are in the region of 450-540 nm (Fig. 4). The temperatures of 5% weight loss of P1 and P2 in TGA are observed at 475 °C and 448 °C, respectively (Fig. 5 & 6). According to DSC, the glass transition temperatures of p1 and P2 are at

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above 400 nm

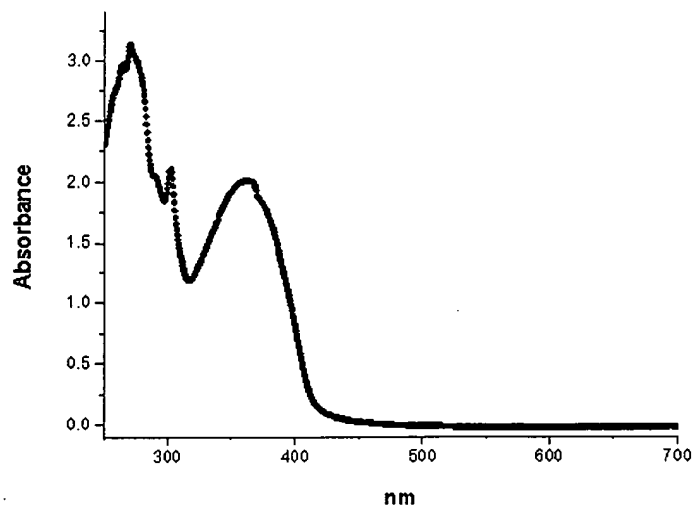


Figure 3:3-UV-VIS spectra spectrum

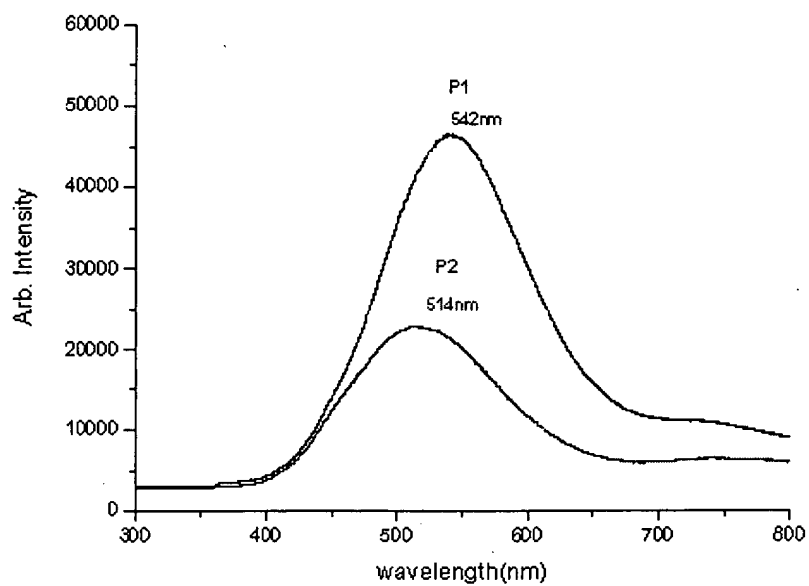


Figure 4:4. Photoluminescence spectra spectrum

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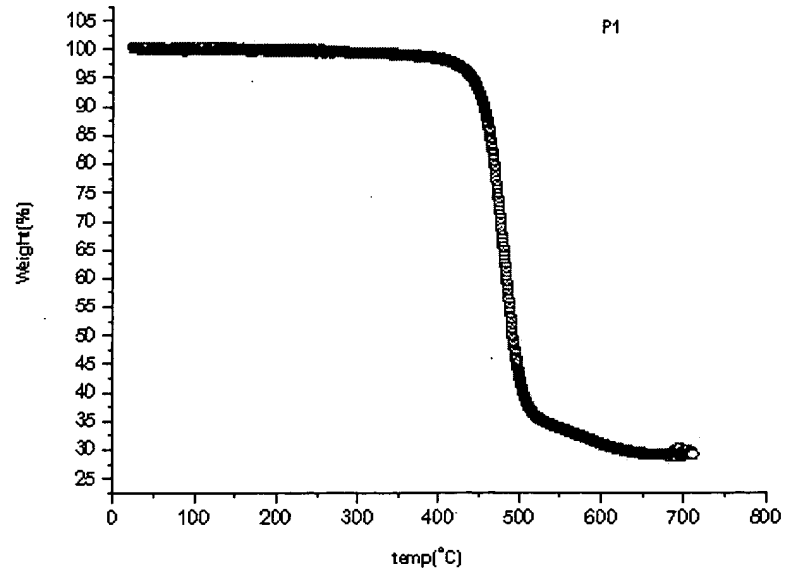


Figure-5. 5:TGA of P1

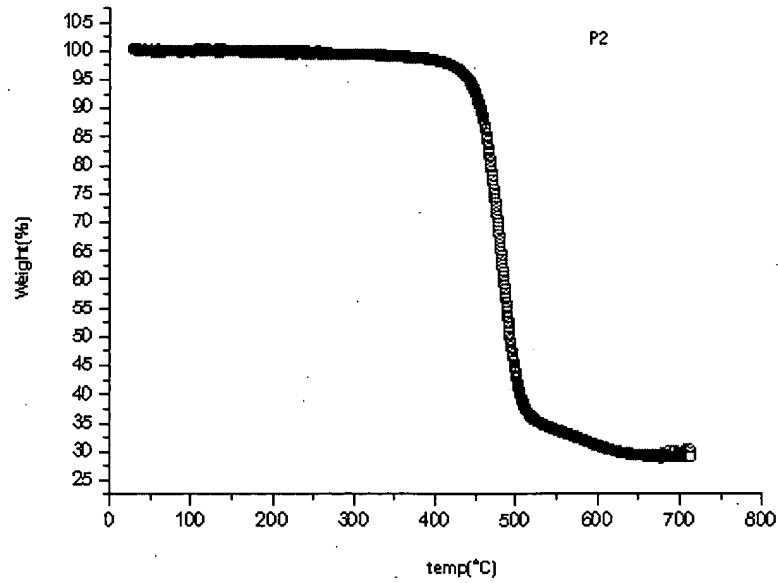


Figure-6. 6:TGA of P2

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The polymers synthesized, as described above, have ~~phase~~ high thermal stability and ~~thus would have a long life time while~~ maintaining the efficiency of light emission. In fabricating devices, the polymers can be coated on an electrode by spin-coating or ink-jetting. They can also increase the compatibility with the polymers of
5 good optical properties (for example, polycarbonate, polymethylmethacrylate and polystyrene). The polymers can be copolymerized with aromatic compounds such as fluorene, benzene, thiophene, carbazole, pyridine, styrene and their respective derivatives.

10 The analytical instruments used are as following. ~~The gel permeation chromatography of Viscotek Co. was used after calibration with polystyrene. The solvent used was tetrahydrofuran (THF). JASCO V-570 for UV-Visible spectrum and Varian Unit Inova 200 (200MHz) for ¹H-MNR were utilized. TGA was determined by TGC 7/7 of Perkin-Elmer Co. under N₂ atmosphere, increasing the temperature by 20~~
15 ~~°C/min. Photoluminescence spectra was obtained by Spectrapro 275i & 300i spectrometer of Acton Co. equipped with CCD camera, using W lamp as a light source. Molecular weight was determined by GPC analysis (Viscotek Co.) using polystyrene standards and THF as solvent at 40 °C. JASCO V-570 and Varian Unit Inova 200 (200 MHz) were used to measure UV-visible and ¹H-NMR spectra,~~
20 ~~respectively. The thermal data of the ladder-polymers were obtained on nitrogen atmosphere at a rate of 20 °C/min by using Perkin-Elmer's TGC 7/7. Fluorescence spectra were obtained with SLM-AMINCO 4800 spectrofluorometer, in which Rhodamin was used as quantum counter.~~

25 The following examples further illustrate the present invention in detail but do not limit the scope thereof.

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Example 1: 9-Vinylbenzyl fluorene.

Fluorenyl lithium was prepared by reacting fluorene (10.0 mmol) with *t*-butyl lithium (1.7 M in *n*-pentane, 10.0 mmol) in THF (10 mL) at $-78\text{ }^{\circ}\text{C}$ for 2 hours.

- 5 Fluorenyl lithium was slowly added to vinyl benzene chloride (10 mmol) in THF solution at $-78\text{ }^{\circ}\text{C}$ and reacted with stirring for 16 hours. Water (100 mL) and ether (100 mL) were added and stirred. Organic layer was extracted, dried and recrystallized to obtain needle shape and ivory colored solids solid.

- $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.77 (2H, d, Fu-H), 7.39-7.20 (10H, m, Fu-H, Bn-H), 6.80-6.66 (1H, q, Vy-H), 5.80-5.70 (1H, d, Vy-H), 5.27-5.21 (1H, d, Vy-H), 4.23 (1H, t, Fu-H), 3.10 (1H, d, Bz).
- 10

Example 2: Polyvinylbenzyl dibromofluorene

- 15 Under N_2 atmosphere, polyvinylbenzyl chloride (1.57 g, M_w 55,000) is dissolved in THF (20 mL). Dibromofluorene (3.24 g) was dissolved in THF (50 mL) and cooled to $-78\text{ }^{\circ}\text{C}$. To this solution, 4 mL of *n*-butyl lithium (2.5 M, *n*-hexane solution) was added and the resulting solution was added slowly to the above polyvinyl benzene chloride solution. The mixture was stirred at room temperature for
- 20 6 hours and water was added. The product was extracted with ethyl ether (200 mL) and dried under vacuum. Obtained product was yellow solid. M_w : 272900. MWD: 5.71. UV-Vis (λ_{max} , THF): 298 nm.

Example 3: Polyvinylbenzyl fluorene

- 25 Under N_2 atmosphere, Polyvinylbenzyl chloride (1.57 g, M_w 55,000) was dissolved in THF (20 mL). Fluorene (1.67g) was dissolved in THF (50 mL) and

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cooled to $-78\text{ }^{\circ}\text{C}$. To this solution added was 4 mL of *n*-butyl lithium (2.5 M, *n*-hexane solution). The resultant solution was added to the above polyvinyl benzyl chloride solution. The mixture was stirred for 6 hours at room temperature and water was added. The product was extracted with ethyl ether (200 mL) and dried under vacuum. Yellow solid was obtained.

M_w : 68160. MWD: 2.96. UV-Vis (λ_{max} , THF): 302 nm.

Example 4: Polyvinylbenzyl-polyfluorene (P1)

Under N_2 atmosphere, polyvinylbenzyl fluorene (1.57 g, M_w 55,000) and dihexylfluorene (3g) were dissolved in chloroform (20 mL). To the solution FeCl_3 (5g) was added and stirred for 4 hours at room temperature. To the mixture methanol was added and the produced precipitates were filtered. The obtained solids were dissolved in THF and the insoluble solids were discarded. The THF solution was dried under vacuum, and yellow solid was obtained.

M_w : 79040. MWD: 2.94. UV-Vis (λ_{max} , THF): 362 nm. PL (λ_{max} , THF): 542 nm. TGA (5%, $^{\circ}\text{C}$): 475, Glass transition temperature($^{\circ}\text{C}$): 421.8.

Example 5: Polyvinylbenzyl-polyfluorene (P2)

Under N_2 atmosphere, polyvinyl benzyl dibromofluorene (1.57g, M_w 55,000) and dihexylfluorene(3g) were dissolved in chloroform(20 mL). To the solution FeCl_3 (5g) was added and stirred for 4 hours at room temperature. To the mixture methanol was added and the produced precipitates were filtered. The obtained solids were dissolved in THF and the insoluble solid was discarded. The THF solution was dried under vacuum, and yellow solid was obtained.

M_w : 132200. MWD: 2.07. UV-Vis (λ_{max} , THF): 362 nm. PL (λ_{max} , THF):

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514 nm. TGA (5%, °C): 448, Glass transition temperature (°C): 404.4.

Example 6: Polyvinylbenzyl-polyfluorene (P3)

Under N₂ atmosphere, polyvinyl benzyl dibromofluorene (1.57 g, M_w 55000) and dihexylfluorene (3 g) were dissolved in benzene (20 mL). To the solution Pd(PPh₃)₄ (5 g) was added and refluxed for 6 hours. To the mixture, methanol was added and the resultant precipitates were filtered. The obtained solid was dissolved in THF, and the insoluble solid was discarded. The THF solution was dried under vacuum, and yellow solids were obtained.

M_w: 159300. MWD: 4.34. UV-Vis ((λ_{max}, THF): 330 nm. PL (λ_{max}, THF): 445 nm.

Example 7: Polyvinylbenzene-poly(fluorene-co-thiophene) (P4)

Under N₂ atmosphere, polyvinyl benzyl dibromofluorene (500 mg, M_w 55000) and 3-octylthiophene (2 g) were dissolved in chloroform (20 mL). To the solution FeCl₃ (2.5 g) was added and stirred for 4 hours at room temperature. To the mixture, methanol was added and the produced precipitate was ~~precipitates were~~ filtered. The obtained solid was dissolved in THF, and the insoluble solid was discarded. The THF solution was dried under vacuum, and ~~obtained~~ yellow solid was obtained.

M_w: 8911. MWD: 3.14. UV-Vis ((λ_{max}, THF): 405 nm. PL (λ_{max}, THF): 544, 682 nm. TGA (5%, °C): 280. Glass transition temperature (°C): 384.8

Example 8: Syndiotactic polyvinylbenzyl fluorene

Under N₂ atmosphere, 1-vinyl-4-(1-fluorenyl)methylbenzene (0.52g) was

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added into a flask and dissolved in toluene (20 mL). To the solution, 12.1 mmol of MAO (2.43 mg, 5 mL) was added slowly and stirred for 30 minutes. 10 mmol of CpTiCl_3 (2.19 mg) was dissolved in 1 mL of toluene and added slowly to the solution at room temperature. After addition, the mixture was stirred for one hour at room
5 temperature and poured into a 200 mL of acidic methanol to obtain solid product. The product was washed with methanol, and dried under vacuum for several hours and 0.3 g of copolymer was obtained. M_w : 2500.

Example 9: Syndiotactic polyvinyl benzyl fluorene-co-styrene (P5)

10 Under N_2 atmosphere, styrene (2.1 g) and 1-vinyl-4-(1-fluorenyl)methylbenzene (0.52 g) were added into the flask and dissolved in toluene (20 mL). To the solution, 12.1 mmol of MAO (2.43 mg, 5mL) was added slowly and stirred for 30 minutes. 10 mmol of CpTiCl_3 (2.19 mg) was dissolved in 1mL of toluene and added slowly to the above solution at room temperature. After addition,
15 the mixture was stirred for 2 hours at room temperature and poured into a 200 mL of acidic methanol to obtain solid product. The product was washed with methanol and dried under vacuum for several hours. ~~hours and~~ 2.5 g of P5 was obtained. M_w : 8,000.

Example 10: Syndiotactic polystyrene-polyfluorene (P6)

20 Under N_2 atmosphere, P5 (500 mg. M_w 8000) was dissolved in chloroform (20 mL). To the solution, FeCl_3 (2.5 g) was added and stirred for 4 hours at room temperature. Methanol was added to the mixture and the precipitates were filtered. The solid precipitate was dissolved in THF and the insoluble solid was discarded. The THF solution was dried under vacuum, and yellow powder was obtained.

25 M_w : 4802. MWD: 2.42. UV-Vis (λ_{max} , THF): 353 nm, PL (λ_{max} , THF): 460 nm, TGA (5%, $^{\circ}\text{C}$): 232.8, Glass transition temperature ($^{\circ}\text{C}$): 413.5.

EFFECT OF THE INVENTION

A series of 2-dimensional ladder-type polyfluorenes was prepared by
introducing atatic or syndiotatic polystyrene as the backbone. The ladder-type
5 polyfluorenes have a high T_g more than 400 °C and excellent thermal stability. No
remarkable aggregation of interchains was observed in the ladder polyfluorene
having syndiotactic polystyrene as the backbone. Accordingly, the polymers can be
utilized as blue light-emitting applications such as display devices, household electric
appliances and cellular phones. As described in details above, the blue light-emitting
10 polymers have a high glass transition temperature and a high temperature of 5%
weight loss. Accordingly, the polymers can be utilized as blue light-emitting materials
in the display devices as well as light-emitting cases of household electric appliances
and light-emitting cases of cellular phones.

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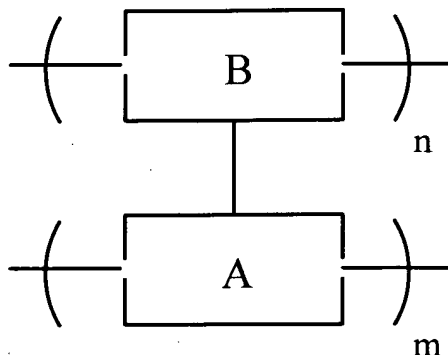
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CLAIMS

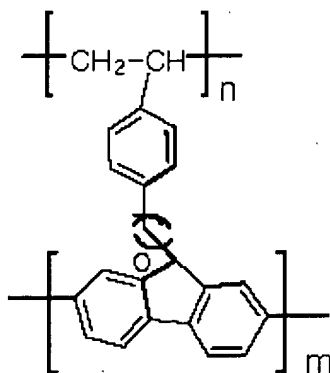
We claim:

1. A blue light-emitting polymer with ladder-type structure represented by the following formula: ~~formula:~~



~~In the formula,~~ wherein A is selected from polyfluorene, polythiophene, polypyrrole, polycarbazole, polyphenylene, polyaniline, polypyridine; B is selected from polystyrene, polypyrrol, polycarbonate, polythiophene, polyphenylene, polyaniline, polypyridine, polycarbazole; n is an integer of 5 to 100; and m is an integer of 2 to 100.

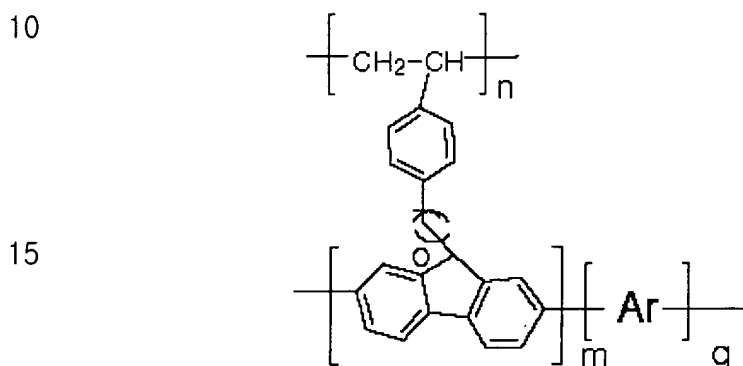
2. The blue light-emitting polymers to claim 1, wherein A is polyfluorene with the following formula and B is polystyrene: ~~polystyrene.~~



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In the formula, wherein n is an integer of 5 to 100; and m is an integer of 2 to 100.

- 5 3. The blue light-emitting polymers to claim 2, wherein Ar is aromatic compounds such as fluorene, fluorene derivatives, benzene, benzene derivatives, thiophene, thiophene derivatives, carbazole, carbazole derivatives, pyridine or pyridine derivatives: ~~derivatives~~.



20 In the formula, wherein n is an integer of 5 to 100; m is an integer of 2 to 100; and q is an integer of 2 to 100.

4. The blue light-emitting polymers to claim 2 or 3, wherein B is the polystyrene specifically with atactic or syndiotactic structure:

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ABSTRACT

The invention relates to the ladder-type and blue light-emitting polymers with excellent thermal ~~heat~~ stability, which are prepared by either ~~polymerized either~~ grafting with blue luminescent monomers on the polymer backbones or
5 polymerization of ~~adding fluorine to~~ styrene monomers derivatives containing fluorene. The above blue light-emitting polymers have a high glass transition temperature and a 5%-weight-loss temperature above 400 °C. Accordingly these polymers can be used as blue luminescent materials in display devices, ~~devices and as~~ ~~luminescent cases for~~ home appliances or cellular phones.

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